

anhydride(acid value:1,011mgKOH/g), and 6g of triethylamine were reacted at 85°C for 10 hours in a round bottom flask equipped with a stirrer and a cooler to obtain a carboxyl-containing terminal alcohol compound(hydroxyl value:57mgKOH/g, acid value: 57mgKOH/g). 348.4g of tolylene diisocyanate(a mixture of 2,4-compound and 2,6-compound, same hereinafter)was added to the above product to react at 85°C for about 15 hours until the isocyanate group fell down to 1.82% in concentration. Then, 239.2g of 2-hydroxyethyl acrylate and 1.3g of methoxy phenol were added to react at 85°C for about 10 hours. The reaction was terminated when the isocyanate fell down to 0.3% in concentration, to obtain a urethane oligomer (A-1) having a weight-average molecular weight of about 6,000(by the GPC) and an acid value of 44mgKOH/g.

Synthesis Example 2

A synthesis was carried out as in Synthesis Example 1, but 2,160g of polytetramethylene glycol, 436.2g of pyromellitic acid anhydride, 6g of triethylamine, 348.4g of tolylene diisocyanate, 239.2g of 2-hydroxyethyl acrylate and 1.3g of methoxy phenol were used, to obtain a urethane acrylate (A-2) having a weight-average molecular weight of about 7,500(by the GPC) and an acid value of 70mgKOH/g.

Synthesis Example 3

1,000g of polytetramethylene glycol (hydroxyl value:112.2mgKOH/g, M.W.:1,000), 124g of ethylene glycol, 437.6g of pyromellitic acid anhydride(acid value:1,011mgKOH/g), 10g of triethylamine and 489g of carbitol acetate were reacted at 85°C for 10 hours to obtain a carbitol acetate mixture(hydroxyl value of the solid:71.4mgKOH/g, acid value: 142.8mgKOH/g) of the terminal alcohol compound having an average of four carboxyl groups in the molecule. 261g of tolylene diisocyanate was added to the above product to react at 85°C for about 15 hours until the isocyanate group fell down to 2.29% in concentration. Then, 122g of 2-hydroxyethyl acrylate and 1.2g of p-methoxy phenol were added to react at 85°C for about 10 hours. The reaction was terminated when the isocyanate fell down to 0.3% in concentration, to obtain the 20% diluted product of an urethane oligomer carbitol acetate (A-3). The solid had an acid value of 115.2mgKOH/g.

Synthesis Examples of urethane (meth)acrylate (A')

Synthesis Example 4

150g of 6% aqueous triethylamine solution was added dropwise to 100g of the urethane oligomer (A-1) obtained in Synthesis Example 1 under stirring to obtain a water-soluble urethane oligomer (A'-1) having a weight-average molecular weight of about 6,200 (by the GPC).

Synthesis Example 5

210g of 6% aqueous triethylamine solution was added dropwise to 100g of the urethane oligomer (A-2) obtained in Synthesis Example 2 under stirring to obtain a water-soluble urethane oligomer (A'-2) having a weight-average molecular weight of about 7,800 (by the GPC).

Example for synthesizing an unsaturated group-containing polycarboxylic acid resin (B)

Synthesis Example 6

380 parts of a bisphenol F type epoxy compound (epoxy equivalent weight: 950g/eq, softening point: 85°C) which is shown by Formula (1) wherein X is -CH₂- and n (an average degree of polymerization) is 6.2 and 925 parts of epichlorohydrin were dissolved in 462.5 parts of dimethyl sulfoxide, followed by adding 60.9 parts of 98.5% NaOH(1.5 mol) under stirring at 70°C for 100 minutes. The reaction was carried out at 70°C for another 3 hours. After the reaction terminated, the reaction solution was washed with 250 parts of water. After the separation of oil and water, the separated oil layer was distilled to recover the most dimethyl sulfoxide and the excessive unreacted epichlorohydrin under reduced pressure and then to remove dimethyl sulfoxide by distillation. The reaction product